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Solid State Microelectrochemical Devices: Transistor and
Diode Devices Employing a Solid Polymer Electrolyte

by

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SOLID STATE MICROELECTROCHEMICAL DEVICES: TRANSISTOR AND DIODE DEVICES EMPLOYING A SOLID POLYMER ELECTROLYTE

Daniel R. Talham, Richard M. Crooks,
Vince Cammarata, Nicholas Leventis,
Martin C. Schloh and Mark S. Wrighton*

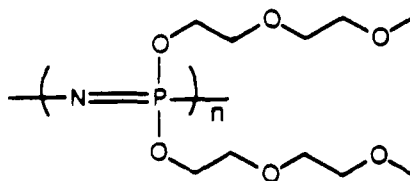
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INTRODUCTION

Not long ago this group first described microelectrochemical devices which are based on microfabricated arrays of electrodes connected by electroactive materials.¹ Because the active components of these devices are chemical in nature, many of these devices are chemically sensitive and comprise a potentially useful class of chemical sensors. Devices showing sensitivity to pH, O₂, H₂, Li⁺, and Na⁺ have been demonstrated.^{2,3} These devices are typically operated in fluid solution electrolytes. If this class of devices is to be useful as gas sensors, systems which are not dependent on liquid electrolytes need to be developed. We have recently reported solid state microelectrochemical transistors which replace conventional liquid electrolytes with polymer electrolytes based on polyethyleneoxide (PEO) and polyvinylalcohol (PVA).⁴ In this report, we discuss additional progress toward solid state devices by employing a new polymer ion conductor based on the polyphosphazene comb-polymer, MEEP⁵ (shown below). By taking advantage of polymer ion conductors we have developed microelectrochemical devices where all of the components of the device are confined to a chip.

Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]

MEEP/LiCF₃SO₃ (4:1)



*Author to whom correspondence should be addressed.

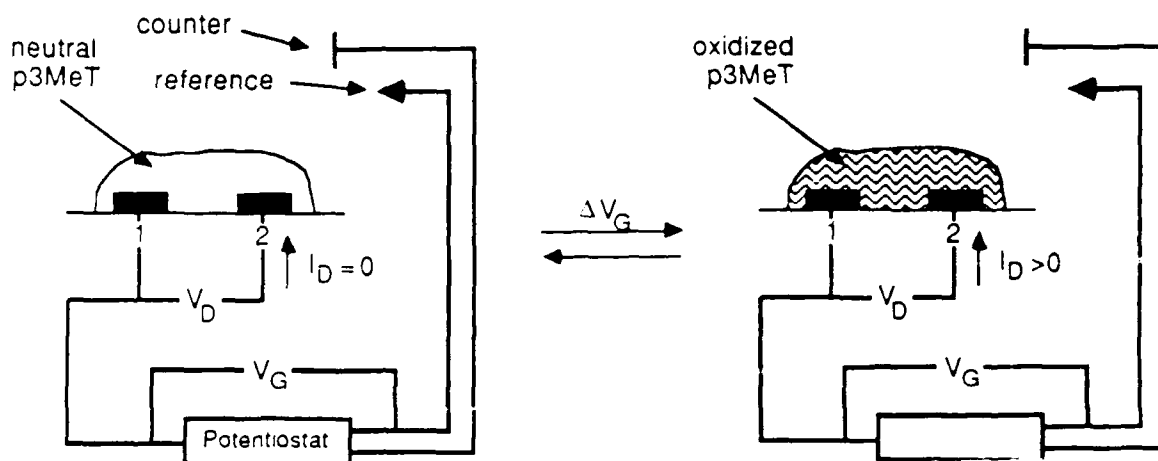


Figure 1. A conducting polymer based microelectrochemical transistor. P3MeT connects two wires of a microfabricated array. Electrodes 1 and 2 are source and drain, respectively. At left, V_G is such that the polymer is neutral and the device is "off", $I_D = 0$. Switching V_G to an oxidizing potential (right) turns the device "on", $I_D > 0$.

MICROELECTROCHEMICAL TRANSISTORS

Figure 1 shows a cross-sectional view of a conducting polymer-based microelectrochemical transistor. Two electrical contacts, the source and drain, are connected by an electroactive material whose resistance can be varied as a function of its state of charge. In the example in Figure 1, the electroactive material is the conducting polymer poly(3-methylthiophene), p3MeT, which in its neutral state is insulating but when oxidized becomes conducting. A small bias, V_D , is applied between the source and the drain resulting in a drain current, I_D , depending on the state of charge of the conducting polymer. For a given V_D , I_D can be varied by changing the gate potential, V_G , of the system which in these devices is electrochemical potential. The faradaic current required to switch the device is the gate current, I_G . The device output is usually represented as a plot of I_D vs. V_G for a constant V_D . This representation provides a measure of the relative conductivity of the conducting polymer as a function of electrochemical potential for small values of V_D .

In our devices, the source and drain are microfabricated wires typically $\sim 70 \mu\text{m}$ long \times $\sim 2.4 \mu\text{m}$ wide \times $\sim 0.1 \mu\text{m}$ high.⁶ An array of eight gold or platinum microelectrodes with interelectrode spacing of $1.4 \mu\text{m}$ is fabricated on a $3 \text{ mm} \times 3 \text{ mm}$ chip.^{1,6} The switching speeds of these devices are enhanced by small electrode spacings.⁶ In addition, reduced spacing between electrodes and small electrode area permit studies in solid electrolyte systems where the resistances are typically much higher than in liquid electrolyte solutions.

SOLID STATE MICROELECTROCHEMICAL DEVICES

Polymer Electrolytes

Preparation of solid state electrochemical devices require that conventional fluid solution electrolytes be replaced with a solid ion conductor. Solid electrolytes have been widely studied primarily for the development of high energy-density batteries.⁷ Classes of solid state electrolytes include classical solids such as the β -aluminas, polyelectrolytes such as Nafion, gel electrolytes and polymer electrolytes.⁷ For the purpose of developing solid state electrochemical devices, polymer electrolytes are promising because they are easily confined to microelectrochemical arrays and are gas permeable.

For application to the surface of the device, the polymer and electrolyte are codissolved in a spreading solvent. After evaporation of the solvent the polymer electrolyte remains as a thin film. The concentration of the salt in the polymer is expressed as a ratio of the number of polymer repeat units per unit of salt. In these studies, the MEEP/ LiCF_3SO_3 ratio is 4:1 or 5:1.⁵ The ionic conductivity of these polymer electrolytes is thought to be due to ion hopping between Lewis base sites along and between chains. This process is facilitated by small amounts of a coordinating solvent.⁸ The devices described here are operated in the presence of some solvent vapor. Usually 20 μl of THF per 50 ml N_2 atmosphere over the device is added as a plasticizer.

Transistor Devices

A schematic of a solid state p3MeT transistor employing the MEEP/ LiCF_3SO_3 electrolyte is shown in Figure 2. Ag plated onto one microelectrode serves as a reference electrode, and a small amount of Ag epoxy close to the array serves as the counter electrode. Alternatively, Ag epoxy can be used as both reference and counter electrode. Monomeric 3-methylthiophene is polymerized electrochemically onto electrodes 2-4 in $\text{CH}_3\text{CN}/0.1 \text{ M } (n\text{-Bu}_4\text{N})\text{ClO}_4$.⁹ The polymer is confined to these electrodes by holding the other electrodes in the array at a reducing potential to discourage polymer growth. The device is characterized before and after the addition of the MEEP electrolyte. This permits comparison of the device characteristics in solution and in the polymer electrolyte. Cyclic voltammetry at each of the derivatized electrodes in $\text{CH}_3\text{CN}/0.1 \text{ M } \text{LiCF}_3\text{SO}_3$ is shown on the left side of Figure 2. The magnitude of the current is the same whether scanning the derivatized electrodes together or individually, showing that the p3MeT connects the electrodes. Cyclic voltammetry of the same array now employing MEEP/ LiCF_3SO_3 electrolyte is shown on the right side of Figure 2. The shape of the curves is essentially the same as in solution electrolyte. The currents are smaller due to the slower scan rates and reduced counterion mobility in the polymer.

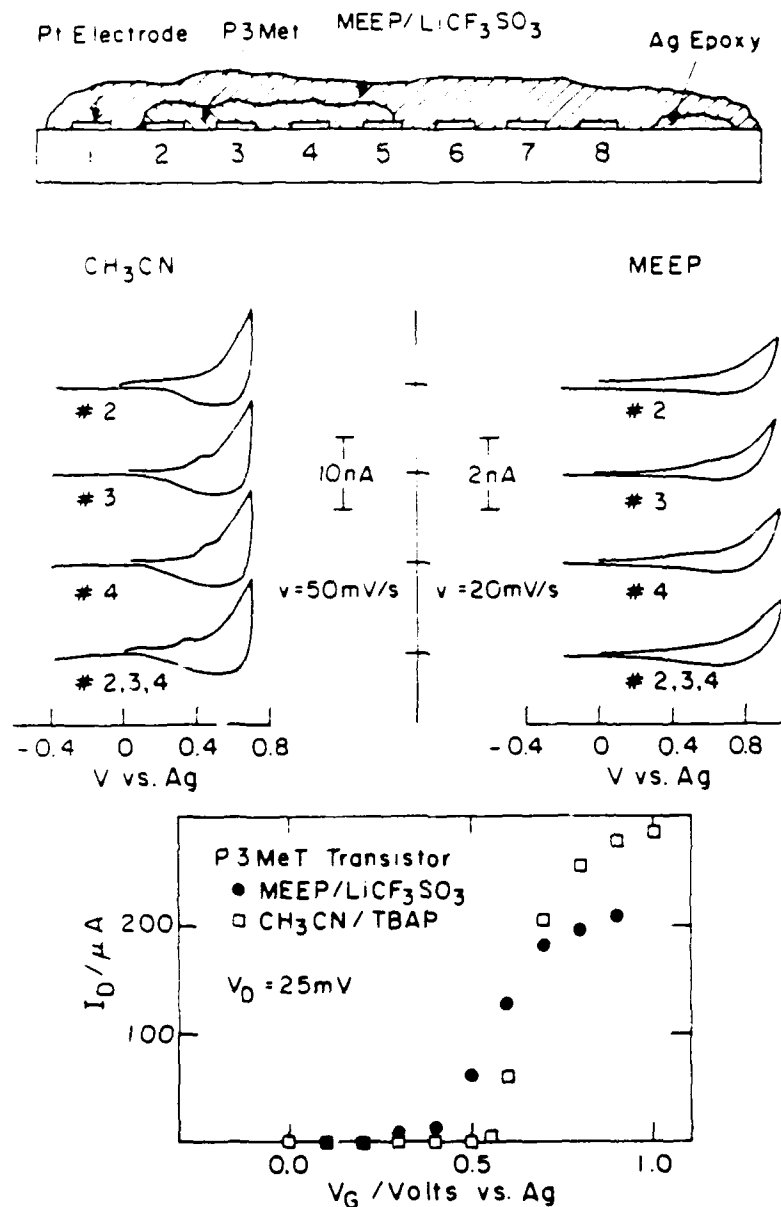


Figure 2. **Top.** Schematic of a p3MeT-based solid state microelectrochemical device. **Center.** Cyclic voltammetry at the p3MeT derivatized electrodes. At left, the device is characterized in the solution electrolyte CH₃CN/0.1 M LiCF₃SO₃ before the application of MEEP. At right, the same device is characterized under MEEP/LiCF₃SO₃ (5:1). **Bottom.** Comparison of the steady-state I_D vs. V_G of the p3MeT device in fluid solution electrolyte and under MEEP/LiCF₃SO₃. Electrodes 3 and 4 are source and drain respectively (see Figure 1).

The steady state I_D vs. V_G characteristics of the pMEd device in both solution and polymer electrolytes are compared in Figure 2. At gate potentials where the polymer is neutral the device is "off", but it turns "on" when V_G is moved positive to an oxidizing potential. There are two key points. First, the drain current of the device in the "on" state is nearly the same under the polymer electrolyte as it is in the solution electrolyte. Second, the transistor device amplifies small electrochemical signals, an important feature of all transistors. This is particularly important in solid electrolytes where diffusion coefficients are small. When the device is turned on, the leakage current through the gate is very small (~ 1 nA) when the I_D is ~ 200 μ A. However, the gain is restricted to very low frequency because electrochemical switching is very slow.⁴

WO_3 is an example of another class of electroactive material, metal oxides, which has been used to construct microelectrochemical devices.¹⁰ WO_3 is a wide band gap semiconductor with high resistance in its neutral state.¹¹ Upon reduction, WO_3 intercalates cations such as H^+ , Li^+ , and Na^+ and becomes conducting. WO_3 -based transistors showing sensitivity to pH and to Li^+ concentration have been demonstrated in solution electrolytes.³ A schematic of a MEEP/ WO_3 device is shown in Figure 3. WO_3 is confined to the required electrodes using standard photolithographic techniques.¹⁰ The transistor characteristics of this device are also presented in Figure 3. At potentials where WO_3 is neutral the device is "off", however at negative potentials WO_3 is reduced and the device turns "on".

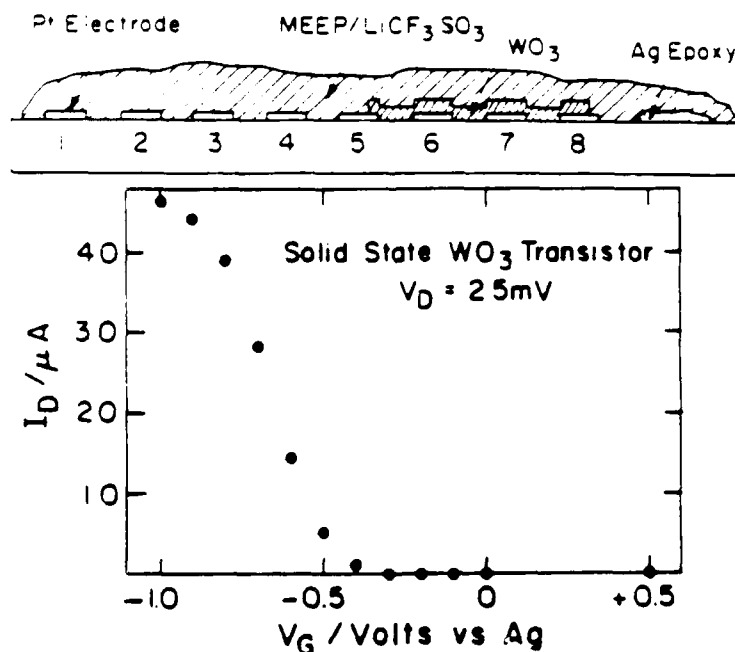


Figure 3. Top. Schematic of a WO_3 -based solid state microelectrochemical device. Bottom. Steady-state I_D vs. V_G of the device diagrammed at top. Electrodes 6 and 7 are source and drain.

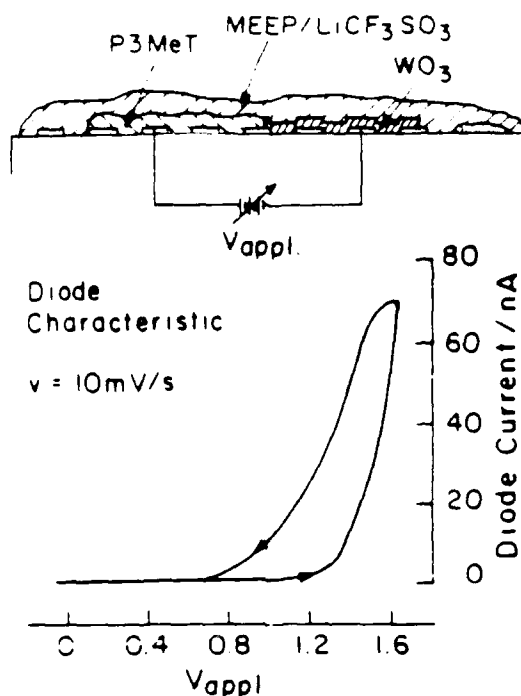


Figure 4. Top. Schematic of a solid state micro-electrochemical diode based on p3MeT and WO₃ under the polymer electrolyte MEEP/LiCF₃SO₃. Bottom. Diode characteristics of the two-terminal device at top. The device turns on when the applied voltage is equal to the difference in redox potentials of the two materials and the bias is such that the p3MeT is oxidized and the WO₃ is reduced. If the bias is reversed (not shown), no current flows.

Diode Devices

By confining both p3MeT and WO₃ to the same array we form the basis of a two-terminal microelectrochemical diode. The underlying principle is that one material, the p3MeT, will only be conducting when it is oxidized, and the other, the WO₃, will only be conducting when reduced. A schematic of the device and the diode characteristic are shown in Figure 4. Current will only flow in the two-terminal device if the magnitude of the applied voltage is equal to the difference in redox potential of the two materials and the bias is such that the conducting polymer is oxidized and the metal oxide is reduced. No current flows when it is reverse biased.

Devices Based on Redox Conduction

Conventional redox polymers can also form the basis of electrochemical transistors.¹² Conventional redox polymers have lower maximum conductivity and yield devices having lower values of I_D than conducting polymers or metal oxides. Conventional redox polymers offer an important design advantage, however. Nearly any stable redox active material can be incorporated into a polymeric system to form a conventional redox polymer. This allows the fabrication of devices with a wide range of chemical sensitivities.

Examples of conventional redox polymer-based devices include those based on viologen, ferrocene and quinone-based redox polymers.¹² Figure 5 shows an example from a new class of solid state microelectrochemical transistors which are based on redox active molecules dissolved in the polymer. The redox active material is N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) which is sublimed into the MEEP/LiCF₃SO₃ film. Here, the MEEP/LiCF₃SO₃ acts as both polymer host and electrolyte. The transistor characteristic of this device is also shown in Figure 5. Below 0.0 V vs. Ag, the device is off, $I_D = 0$, since all the TMPD is neutral. As TMPD is oxidized, the device turns on with a maximum I_D near $E_{1/2}$ of TMPD^{•+}. We have determined the diffusion coefficient for charge transport, D_{CT} , of TMPD^{•+} in MEEP to be 2×10^{-8} cm²/s. It is not clear if the charge transport mechanism is via self-exchange or physical diffusion, but most likely involves both mechanisms. This value of D_{CT} is comparable to those of conventional redox polymers where the redox centers are covalently bonded to the polymer backbone and the sole mechanism of charge transfer is via self-exchange.¹³ The ability to fabricate a solid state microelectrochemical transistor where the active molecules are not required to be covalently attached to a polymer backbone suggests a wide range of new devices. Of particular interest is the prospect of including chemical sensitive molecules into this class of device for potential use as gas sensors.

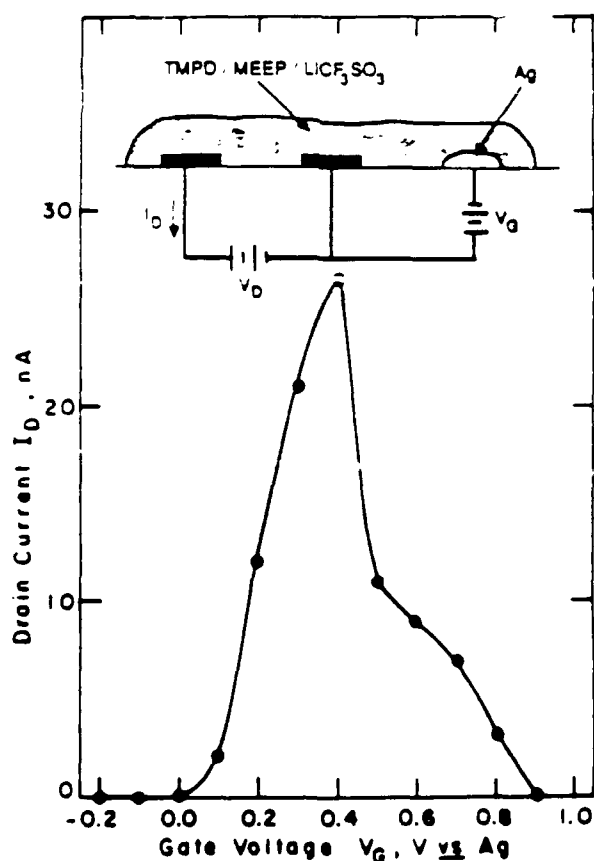


Figure 5. Schematic and transistor characteristic of a new class of microelectrochemical device which is based on a redox active material dissolved in a polymer ion conductor. Here, TMPD is sublimed into and saturates the MEEP/LiCF₃SO₃ film. The drain voltage, V_D , is 25 mV.

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